

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number
WO 01/97968 A2(51) International Patent Classification⁷:

B01J 23/00

(74) Agent: LE ROUX, Marius; D.M. Kisch Inc., P.O. Box 781218, 2146 Sandton (ZA).

(21) International Application Number: PCT/ZA01/00084

(22) International Filing Date: 20 June 2001 (20.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/212,927 20 June 2000 (20.06.2000) US

(71) Applicant (for all designated States except US): SASOL TECHNOLOGY (PTY) LTD [ZA/ZA]; 1 Sturdee Avenue, Rosebank, 2196 Johannesburg (ZA).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ESPINOZA, Rafael, Luis [ZA/US]; 418 Lansbrook Street, Ponca City, OK 74601 (US). BROMFIELD, Tracy, Carolyn [ZA/ZA]; 2 Melrose Place, Cnr. Delius and Chopin Street SW5, 1911 Vanderbijlpark (ZA). BOTES, Frederick, Gideon [ZA/ZA]; 12 Vaalriver Street SE4, 1911 Vanderbijlpark (ZA). VISAGIE, Rentia [ZA/ZA]; 23 Donkin Street, 9570 Sasolburg (ZA). LAWSON, Keith, Henry [GB/ZA]; 12 Lategan street, 9570 Sasolburg (ZA). GIBSON, Philip [ZA/ZA]; 18 Zoutpansberg Street, Vaalpark, 9570 Sasolburg (ZA).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/97968 A2

(54) Title: HYDROCARBON SYNTHESIS CATALYST AND PROCESS

(57) Abstract: According to the present invention there is provided a hydrocarbon synthesis catalyst comprising a precipitated iron product and a catalyst promotor. The catalyst has a surface area of below 60 m² per gram of catalyst in the reduced form or below 100 m² per gram of catalyst in the non-reduced form. According to the invention there is also provided a process for preparing the catalyst and the use thereof in the synthesis of hydrocarbons.

HYDROCARBON SYNTHESIS CATALYST AND PROCESS

Field Of The Invention

5

The invention relates to a hydrocarbon synthesis catalyst and the preparation thereof. The invention also relates to the use of said catalyst in a process for the synthesis of hydrocarbons.

10 Background Of The Invention

A typical hydrocarbon synthesis process, such as the Fischer-Tropsch process, involves the hydrogenation of CO in the presence of Group VIII metals such as Fe, Co, and Ru. The products formed from this reaction are gaseous, liquid and 15 waxy hydrocarbons as well as oxygenates that include, *inter alia*, olefins and paraffins. The carbon distribution of these products is described by the Anderson-Schulz-Flory distribution.

20 Fused iron catalysts are known in the prior art to be used in Fischer-Tropsch synthesis. They are generally used in fluidized bed systems which operate at high temperatures. Such a fluidized bed system may include a fixed fluidized bed reactor.

Processes of this character, wherein fluidized solids are contacted with gases, have a number of inherent and important advantages. For example, intimate contact between the gases and the fluid subdivided solids is secured. It is also possible to maintain a substantially uniform temperature throughout the bed as 5 a result of the extremely rapid transfer of heat from one section of the bed to the other because of the rapid circulation of the fluid subdivided solids. Furthermore, due to the rapid transfer of heat between the solids under these conditions, it is possible to readily add or remove heat from the system at an extremely rapid rate.

10

In these fluidized reactions the subdivided solids or catalysts usually have a particle size in the range of from about 1 to 200 microns. These particles are suspended in a fluid ebullient state by means of the up flowing suspending gases, the velocity of which may vary.

15

The fused catalyst have a high mechanical strength, which is higher than that of precipitated catalysts. The strength of the catalysts is essential, as there is rapid mixing in a fluidized bed system. Fluidized beds are also operated at high temperatures (280 – 350°C) so that the products are all gaseous. 20 Unfortunately, carbon formation and deposition on the catalyst also occur at these elevated temperatures. The deposited carbon originates from the CO in

the synthesis gas. This deposition causes the catalyst particle to swell and disintegrate and eventually requires the replacement of the catalyst as the swelling particle and additional fine material creates an expansion of the fluidized bed. Temperature control and the control of the entire synthesis 5 reaction substantially deteriorates due to poor catalyst fluidization.

A number of workers in this field have proposed various methods of improving the fluidizing characteristics of the solid iron catalyst in view of its affinity to form carbon during the synthesis process. For example in US 2,459,444 the 10 invention described therein claims a method of improving the fluidizing characteristics of the powdered iron catalyst for the synthesis of hydrocarbons by mixing with the iron a quantity of a coarser or larger particle size powdered inert material such as silica gel. Whereas, on the other hand, US 2, 471,913 proposes the use of an inert solid siliceous diluent in the synthesis zone "in 15 order to maintain fluidity of the catalyst".

The fused iron catalyst can be prepared from low impurity iron sources, for example, presently Sasol uses millscale from a steelworks to prepare its Synthol catalyst. The disadvantage of using such a material is that the supply is 20 dependent on the throughput of the steelworks and the impurity levels in the millscale are not always consistent.

One disclosure in the prior art: US 2, 758,128, relates to a carrier free iron catalyst which is prepared by means of forward precipitation and is suitable for hydrogenation of carbon monoxide with the production of a high yield of low 5 boiling gasoline-like hydrocarbons.

The technique of forward precipitation described in this patent entailed addition of an iron salt solution (also including copper and lime) to a boiling soda solution. The precipitated catalyst was impregnated with a promotor and was 10 then dried at 105°C, crushed and reduced. The reduced catalyst so formed had a desired large inner surface of 110 to 180m²/per gram of iron which is achieved mainly by using the precipitation method. The patent further reveals that the catalyst may be used in the carbon monoxide hydrogenation with the use of "fixed beds" as well as in hydrocarbon synthesis operated with the catalyst 15 suspended in liquid media (or "slurry process"). However, it is specifically stated therein that the application of a catalyst prepared according to that particular invention in the "fluidized process" is not possible.

Precipitated iron catalysts are generally known to be not suitable for high 20 temperature operation due to their high specific activity related to the high surface areas and large pore volumes. The strength of precipitated catalysts

generally does not match the strength of fused catalysts.

In US 4,340,503, a method of preparation of a supported iron catalyst is described wherein a silicate support substantially free of aluminum is

5 impregnated with iron and potassium and the material is capable of converting synthesis gas to C₂ – C₄ olefins. The catalyst is said to be suitable for operation in a fluidized bed reactor as would be expected for a supported impregnated material.

10 Certain components of a fused iron catalyst which are inherited from the metal parent ore are not desirable in certain instances, for example, Al₂O₃. Whenever Al₂O₃ is in excess of certain amounts, it provides too much acidity to the catalyst and therefore the synthesis process results in an increased production of the paraffins.

15

The inventors of the present invention have now developed a precipitated iron catalyst which is capable of hydrogenating carbon monoxide in a fluidized bed process. Such an unsupported precipitated catalytic material should ideally still be suitable to withstand the turbulent dynamics of a fluidized bed reactor

20 without negatively affecting its performance, which should be comparable to that of a fused iron catalyst, but with reduced affinity for carbon formation during

the synthesis process. Such a precipitated catalytic material should ideally comprise none or predetermined minimal amounts of impurities unlike the fused iron catalyst.

5 Summary Of The Invention

According to a first aspect of the present invention there is provided a reduced hydrocarbon synthesis catalyst comprising a precipitated iron product in the form of iron and/or an iron composition; at least one catalyst promotor; and the 10 reduced catalyst being characterized therein that it has a surface area of below 60m² per gram of catalyst.

The catalyst may be suitable for use in a high temperature Fisher-Tropsch process and preferably it is suitable for use in a fluidized bed system, preferably 15 a fixed fluidized bed system.

The precipitated iron product may be the product formed due to the precipitation of an iron salt. The iron salt may comprise a salt selected from the group consisting of iron nitrate; iron oxalate; iron sulphate and iron chloride. In one 20 preferred embodiment of the invention it comprises iron nitrate.

The iron salt may be precipitated from an aqueous solution.

The precipitated iron product may be precipitated in the presence of an alkali.

5 The alkali may comprise a hydroxide. The alkali may comprise carbonate compound. In one embodiment of the invention it comprises ammonium hydroxide.

10 The precipitated iron composition may comprise an iron oxy hydroxide which at least partly converts to an iron oxide upon drying which in turn at least partly converts to iron upon reduction. Accordingly, in the reduced form of the catalyst the iron product comprises at least some iron.

15 The catalyst promotor may comprise a source of an alkali metal and/or an alkaline earth metal. Preferably it comprises an alkali metal oxide or an alkaline earth metal oxide. The alkali metal oxide may be selected from the group consisting of Na_2O , K_2O and Cs_2O . In one embodiment of the invention it may comprise K_2O .

20 The concentration of the catalyst promotor in the catalyst may be varied to maximize the activity and selectivity of the catalyst.

Where K_2O is the promotor, K_2O may be present at a concentration from 0.01g K_2O /100g Fe to 2.0g K_2O /100g Fe, preferably from 0.05g K_2O /100g Fe to 1.0g K_2O /100g Fe, preferably about 0.1 to 0.5g K_2O /100gFe.

- 5 The surface area of the reduced catalyst may be smaller than 50m²/g catalyst, preferably 30m²/g catalyst or smaller; preferably 20m²/g catalyst or smaller; and even 10m²/g catalyst or smaller. The said surface area will normally not be smaller than 1m²/g catalyst.
- 10 The surface area may be determined by the classical method of Brunauer, Emmet and Teller (BET) which makes use of nitrogen adsorption isotherms. It will be appreciated that outer and inner "exposed" surface areas are measured.
- 15 The catalyst may also include substantially none or controllable minimal amounts of impurities. This is different to fused iron catalysts prepared from, for example, iron millscale which have variable amounts of impurities, as explained above.
- 20 The impurities may be metal oxides other than the selected promotors which react with alkali metal or alkaline earth metal to form adducts which are undesirable since they are not active for the Fischer-Tropsch process and may

give rise to unwanted products.

The catalyst may contain none or low (preferably consistent) levels of impurities such as Al_2O_3 , SiO_2 , MgO , CaO , Li_2O , Na_2O and TiO_2 preferably Al_2O_3 , SiO_2 ,

5 MgO or CaO . The total amount of impurities may be present in the catalyst at below 5g/100gFe preferably below 2g/100gFe, preferably below 1g/100g Fe.

It has been found that reduced amounts of impurities allow reduced amounts of

promotor (especially K_2O) to be used. In particular, as the level of impurities is

10 reduced, the K_2O promotor dilution in the catalyst matrix, which is dependent on the amount of the impurities present, is also reduced.

There is a tendency for promotor to be consumed in the matrix by combination with impurities to form substantially inert compounds such as potassium silicate,

15 therefore requiring that the amount of promotor [especially K_2O] used in the catalyst preparation stage to be increased to replenish the consumed portion. It is believed that this is not the case when the method of the present invention is applied in contrast to the conventional fused iron catalyst process. Thus the amount of promotor [especially K_2O] that is required to induce the desired 20 promotional effects may also reduce proportionally to the level of impurities.

10

The catalyst may have a particle size from 1 to 250 μm , preferably 2 to 200 μm , preferably about 5 to 150 μm .

The catalyst is a non-supported catalyst.

5

According to another aspect of the present invention there is provided a non-reduced hydrocarbon synthesis catalyst comprising a precipitated iron product in the form of iron and/or an iron composition; at least one catalyst promotor; and the catalyst being characterized therein that it has a surface area below 10 100 m^2 per gram of catalyst prior to reduction.

The non-reduced catalyst may have a surface area from 80 m^2/g catalyst or less, preferably from 50 m^2/g of catalyst or less. The surface area may be from 10 to 80 m^2/g catalyst and even from 10 to 50 m^2/g of catalyst.

15

The non-reduced catalyst may subsequently be reduced to have a surface area of below 60 m^2 per gram of catalyst.

It will be appreciated that the non-reduced catalyst is similar to the reduced

20 catalyst except that it is in a condition prior to reduction.

According to a second aspect of the present invention there is provided a process for preparing a reduced hydrocarbon synthesis catalyst with a surface area of below 60m² per gram of catalyst comprising the steps of –

- precipitating an iron product in the form of iron and/or an iron composition from an iron containing solution;
- 5 - adding at least one catalyst promotor prior, during or subsequent to the precipitation process; and
- subjecting the precipitated iron product to heat treatment to provide the catalyst with a decreased surface area; and
- 10 - subjecting the iron product to reducing conditions to reduce the iron product to metallic iron, the reduced catalyst having a surface area of below 60m² per gram of catalyst.

It is foreseen that reduction and heat treatment may take place at the same time. Preferably however, heat treatment will take place prior to reduction, that is the heat-treated iron product will subsequently be reduced.

The catalyst may be suitable for use in a high temperature Fischer-Tropsch process and preferably it is suitable for use in a fluidized bed system, preferably 20 a fixed fluidized bed system.

The iron containing solution may comprise an aqueous solution and preferably it is a solution of an iron salt. The iron salt may comprise the product as described hereinabove.

- 5 The precipitated iron product may be precipitated in the presence of an alkali. The alkali may be as described hereinabove.

In one embodiment of the invention the iron composition may be precipitated by means of reverse precipitation wherein an alkali is added to the iron containing

- 10 solution. Preferably the alkali is in the form of a solution, preferably an aqueous solution.

In another embodiment of the invention the iron composition may be precipitated by means of forward precipitation wherein the iron containing

- 15 solution is added to an alkali, preferably an alkali solution.

The precipitation temperature and pH may be varied and the two parameters eventually have an influence on the surface area of the final catalyst particles.

- 20 Precipitation may be carried out at a temperature of 0°C to 100°C, typically 10°C to 60°C, and even from 20°C to 40°C. Precipitation may be carried out at

ambient temperature.

The final pH of the solution containing the precipitate may be 5.0 to 9.0, typically 6.0 to 8.0 or even 6.5 to 7.5.

5

In another embodiment of the invention the iron composition may be precipitated at a substantially constant pH wherein the iron containing solution and an alkali are added to each other in order to retain the pH substantially constant, preferably at a range between 6-9, typically at a pH of about 7.5 ± 0.2 .

10

The catalyst promotor may be co-precipitated with the iron product. Alternatively the promotor may be added to the precipitated iron product. The precipitated iron product may be impregnated with the catalyst promotor.

15 The catalyst promotor may comprise a source of an alkali metal and/or alkaline earth metal. The catalyst promotor may be added in the form of a salt of an alkali metal and/or an alkaline earth metal.

20 The heat treatment may be carried out at a temperature from 140°C or higher, preferably from 140 to 600°C, preferably from 300 to 450°C. The heat treatment may be carried out for longer than 15 minutes, preferably longer than

1 hour. The heat treatment may be carried out in air. During the heat treatment the surface area is preferably decreased by at least 20%.

Prior to the heat treatment the catalyst may be dried.

5

In one preferred embodiment of the invention the catalyst may be spray dried.

The spray drying may take place at an inlet temperature between 250 and 500°C preferably between 300 and 400°C preferably at about 350°C. The outlet temperature may be between 80 and 180°C, preferably between 100 and

10 150°C, preferably at about 120°C.

The spray drying process may result in spherical catalyst particles in contrast to the fused catalytic material which is non-spherical and irregular. Spherical particles are generally preferred.

15

The spray dried particles had a particle size from 1 to 250µm, preferably 5 to 150µm.

The reduction process comprises heat treatment under reducing conditions.

20 The reducing conditions may be provided by using a reducing gas such as H₂ and/or CO. The heat treatment may be in excess of 200°C. In the process iron

oxide is reduced to metallic iron.

Preferably at least 70% (mass/mass), preferably at least 80% and more preferably at least 90% of iron is reduced to be in the form of metallic iron.

5 Preferably substantially all iron is reduced to metallic iron.

The catalyst of the present invention may exhibit sufficient mechanical strength to operate in a fluidized bed reactor.

10 The catalyst prepared in accordance with the second aspect of the invention may be fluidisable.

The catalyst of the present invention may exhibit a prolonged useful lifetime due to an unusually low rate of carbon deposition when compared to conventional 15 fluidized Fischer-Tropsch synthesis process and correspondingly, there occurs less expansion of the fluidized bed.

According to another aspect of the present invention there is provided process for preparing a non-reduced hydrocarbon synthesis catalyst with a surface area 20 of below 100m² per gram of catalyst comprising the steps of –
- precipitating an iron product in the form of iron and/or an iron

composition from an iron containing solution;

- adding at least one catalyst promotor prior, during or subsequent to the precipitation process; and
- subjecting the precipitated iron product to heat treatment to provide the catalyst with a decreased surface area which is below 100m² per gram of catalyst prior to reduction.

5

The non-reduced catalyst may have a surface area from 80m²/g catalyst or less, preferably 50m²/g catalyst or less. The surface area is preferably from 10 to 10 80m²/g catalyst and even from 10 to 50 m²/g catalyst.

It will be appreciated that the process for preparing the non-reduced catalyst is the same as that of preparing the reduced catalyst except that the reduction step is omitted.

15

The non-reduced heat treated catalyst may subsequently be subjected to reducing conditions to reduce at least some of the iron product to metallic iron, the reduced catalyst having a surface area below 60m² per gram of catalyst.

20 According to a third aspect of the invention there is provided a hydrocarbon synthesis catalyst prepared by the process substantially as described

hereinabove.

According to a fourth aspect of the invention there is provided a process for the synthesis of hydrocarbon by reacting hydrogen with carbon monoxide in the 5 presence of a catalyst substantially as described hereinabove.

The process for the synthesis of hydrocarbon may be a Fischer-Tropsch process, preferably a high temperature Fischer-Tropsch process. The process may be conducted in a fluidized bed reactor.

10

In a typical embodiment of the invention the process for the synthesis of the hydrocarbons is conducted in a fixed fluidized bed reactor.

15 The process may be carried out at a pressure from 10 to 60 bar (1 and 6 MPa), typically at about 15 to 30 bar, within a temperature range between 250°C and 400°C, typically from 270°C to 370°C, and even from 330°C to 350°C.

The composition of the total synthesis gas feed generally comprises H₂ and CO in an H₂:CO molar ratio in the range of about 5:1 to about 1:5, typically at 4:1.

20

Typically, the feed synthesis gas may also comprise about 1 to 25 volume

percent CO₂, N₂ and/or methane.

The products of the process may comprise a mixture of linear, branched chain and aromatic hydrocarbons. The hydrocarbons may essentially comprise

5 paraffins, olefins and oxygenates.

The invention also relates to the use of a catalyst substantially as described hereinabove in the synthesis of hydrocarbon by reacting hydrogen with carbon monoxide.

10

The invention also relates to hydrocarbons produced by the process substantially as described hereinabove.

The invention will now be further described by means of the following non-

15 limiting examples.

Examples

Example 1

20 Preparation of catalyst by means of reverse precipitation.

A 140ml 25% (w/w) aqueous ammonium hydroxide (NH_4OH) solution was added to 100ml of a 1M aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ containing 0.17 g KNO_3 at ambient temperature whilst stirring rapidly. Precipitation was allowed to occur until a pH of 7.

5

The resulting precipitate was filtered and dried at 120°C for 16 hours.

The dried product was then heat treated in air at 350°C for 4 hours.

Reduction was done at 420°C for 16 hours in the presence of excess hydrogen.

10 The surface area before reduction was $43\text{m}^2/\text{g}$ catalyst.

Example 2

Preparation of catalyst by means of continuous precipitation [constant pH

15 **precipitation].**

A 1 M aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was co-fed with a 25% (w/w) aqueous solution of ammonium hydroxide (NH_4OH) at ambient temperature while stirring rapidly to maintain a constant pH of 7.5. The resulting precipitate 20 was then filtered using a filter press, and washed with distilled water to a conductivity of 60 μS in the wash water effluent stream. After briefly drying with

a nitrogen stream, the product was then homogenized with water to achieve a slurry with a solids content suitable for spray-drying and sufficient KNO_3 added to achieve 0.2g $\text{K}_2\text{O}/100\text{g Fe}$ in the dried product.

- 5 The slurry was spray-dried using a hollow cone nozzle at a pressure of 15 bar, inlet temperature of 350°C and an outlet temperature of 115°C to achieve a particle size distribution of 5-150 μm . The dried product was then heat treated to 350°C in a rotary retort furnace for 4 hours.
- 10 The dried product was then reduced in the same manner as in Example 1.

The surface area before reduction was 41 m^2/g catalyst and subsequent to reduction it was 4 m^2/g catalyst. Before heat treatment it had a surface area of 252 m^2/g catalyst.

15

In the reduced catalyst 100% (mass/mass) of the iron was in the metallic form.

20

Chemical Analysis of Non-Reduced Product

Fe (mass%)	68
(g)Cu/100gFe	0.064
(g)K ₂ O/100gFe	0.14
(g)Cl/100gFe	0.01
(g)SO ₄ /100gFe	0.03

Example 3

5

Preparation of catalyst by means of forward precipitation.

A 1 M aqueous solution of Fe(NO₃)₃.9H₂O was added drop wise to a 1 M aqueous solution of Na₂CO₃ at ambient temperature whilst stirring rapidly until a 10 pH of 7 was reached. Thereafter the mother liquor was removed by filtration and KNO₃ added to achieve 0.2gK₂O/100gFe. The product was then oven-dried at 110°C for 16 hours. Thereafter, the dried product was heat treated in air at 350°C for 4 hours.

15 The dried product was then reduced in the same manner as in Example 1.

The surface area before reduction was 23m²/g catalyst.

The typical chemical composition of the iron nitrate solution used in all three examples was 12,8% (mass%) Fe; 0,57g Mn/100g Fe; 0,002g P/100g Fe; 5 0,045g Cr/100g Fe; 0,047g Ni/100g Fe; 0,044g Al/100g Fe; and 0,057g Cu/100g Fe.

Example 4

10 **Hydrocarbon synthesis**

The catalyst prepared according to example 2 was used in the synthesis of hydrocarbons from CO and H₂ in a fixed fluidized bed reactor

15 The reaction conditions were as follows:

Temperature range: 300-370, usually 330°C

Pressure range: 15-30 bar, usually 20 bar

Total feed H₂/CO [volume/volume] approximately 4

Conversions:

	Per pass (mass%)
CO+CO ₂	59
H ₂ + CO	41

Product selectivity:

Product	Mass %
CH ₄	13
Total C ₂	9.5
C ₂ =/C ₂ -	1.1
C ₃ =/C ₃ -	11.8
Acid make (mg KOH/gH ₂ O)	9

5 No break-up of the catalyst was observed. The catalyst performed comparably to fused iron catalyst but lower carbonization was observed which results in a longer lifetime of the catalyst.

10 It will be appreciated that many variations in detail are possible without thereby departing from the scope and spirit of the invention.

CLAIMS

1. A reduced hydrocarbon synthesis catalyst comprising a precipitated iron product in the form of iron and/or an iron composition; at least one catalyst promotor; and the reduced catalyst being characterized therein that it has a surface area of below 60m² per gram of catalyst.
2. The catalyst of claim 1 wherein the at least one catalyst promotor comprises a source of an alkali metal and/or alkaline earth metal.
3. The catalyst of claim 2 wherein the at least one catalyst promotor comprises an alkali metal oxide.
4. The catalyst of any one of the preceding claims wherein the surface area of the reduced catalyst is less than 50m²/g of catalyst.
5. The catalyst of claim 4 wherein the surface area is 30m²/g of catalyst or less.
6. The catalyst of claim 5 wherein the surface area is 20m²/g of catalyst or less.

7. The catalyst of any one of the preceding claims which includes a total amount of impurities in the form of Al_2O_3 , SiO_2 , MgO and CaO in an amount of below 5g/100g Fe.

5

8. A non-reduced hydrocarbon synthesis catalyst comprising a precipitated iron product in the form of iron and/or an iron composition; at least one catalyst promotor; and the catalyst being characterized therein that it has a surface area below 100m^2 per gram of catalyst prior to reduction.

10

9. The catalyst of claim 8 which has a surface area from $80\text{m}^2/\text{g}$ of catalyst or less.

15 10. The catalyst of claim 9 which has a surface area from $50\text{m}^2/\text{g}$ of catalyst or less.

11. A process for preparing a reduced hydrocarbon synthesis catalyst with a surface area of below 60m^2 per gram of catalyst comprising the steps of
- precipitating an iron product in the form of iron and/or an iron composition from an iron containing solution;
- adding at least one catalyst promotor prior, during or subsequent

20

to the precipitation process; and

- subjecting the precipitated iron product to heat treatment to provide the catalyst with a decreased surface area; and
- subjecting the iron product to reducing conditions to reduce the

5 iron product to metallic iron, the reduced catalyst having a surface area of below 60m² per gram of catalyst.

12. The process of claim 11 wherein the heat treatment is carried out and thereafter the heat treated iron product is subjected to the reducing

10 conditions.

13. The process of either one of claims 11 or 12 wherein an iron composition is precipitated by means of reverse precipitation wherein an alkali is added to the iron containing solution.

15

14. The process of either one of claims 11 or 12 wherein an iron composition is precipitated by means of forward precipitation wherein the iron containing solution is added to an alkali.

20 15. The process of either one of claims 11 or 12 wherein an iron composition is precipitated at a substantially constant pH wherein the iron containing

solution and an alkali are added to each other in order to retain the pH substantially constant.

16. The process of any one of claims 11 to 15 wherein heat treatment is carried out at a temperature from 140°C or higher.
5
17. The process of claim 16 wherein the heat treatment is carried out from 140 to 600°C.
- 10 18. The process of any one of claims 11 to 17 wherein the catalyst is spray dried.
- 15 19. The process of any one of claims 11 to 18 wherein the reducing conditions comprises heat treatment under reducing conditions.
20. A process for preparing a non-reduced hydrocarbon synthesis catalyst with a surface area of below 100m² per gram of catalyst comprising the steps of –
 - precipitating an iron product in the form of iron and/or an iron composition from an iron containing solution;
 - adding at least one catalyst promotor prior, during or subsequent

to the precipitation process; and

subjecting the precipitated iron product to heat treatment to provide the catalyst with a decreased surface area which is below 100m² per gram of catalyst prior to reduction.

5

21. A hydrocarbon synthesis catalyst prepared by the process of any one of claims 11 to 20.

22. A process for the synthesis of hydrocarbon wherein hydrogen is reacted with carbon monoxide in the presence of a catalyst of any one of claims 1 to 10 or 21.

10 23. The process of claim 22 which is a high temperature Fischer-Tropsch process conducted in a fluidized bed reactor.

15

24. The process of claim 23 which is conducted in a fixed fluidized bed reactor.

20 25. The use of a catalyst of any one of claims 1 to 10 or 21 in the synthesis of hydrocarbon by reacting hydrogen with carbon monoxide.

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number
WO 01/97968 A3(51) International Patent Classification⁷: **C10G 2/00**, (74) Agent: LE ROUX, Marius; D.M. Kisch Inc., P.O. Box B01J 23/78, 23/745

(21) International Application Number: PCT/ZA01/00084

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,

(22) International Filing Date: 20 June 2001 (20.06.2001)

AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

(25) Filing Language: English

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

(26) Publication Language: English

GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

(30) Priority Data: 60/212,927 20 June 2000 (20.06.2000) US

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,

(71) Applicant (*for all designated States except US*): SASOL
TECHNOLOGY (PTY) LTD [ZA/ZA]; 1 Sturdee Avenue,
Rosebank, 2196 Johannesburg (ZA).MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,
ZW.(72) Inventors; and
(75) Inventors/Applicants (*for US only*): ESPINOZA, Rafael, Luis [ZA/US]; 418 Lansbrook Street, Ponca City, OK 74601 (US). BROMFIELD, Tracy, Carolyn [ZA/ZA]; 2 Melrose Place, Cnr. Delius and Chopin Street SW5, 1911 Vanderbijlpark (ZA). BOTES, Frederick, Gideon [ZA/ZA]; 12 Vaalriver Street SE4, 1911 Vanderbijlpark (ZA). VISAGIE, Rentia [ZA/ZA]; 23 Donkin Street, 9570 Sasolburg (ZA). LAWSON, Keith, Henry [GB/ZA]; 12 Lategan street, 9570 Sasolburg (ZA). GIBSON, Philip [ZA/ZA]; 18 Zoutpansberg Street, Vaalpark, 9570 Sasolburg (ZA).**Published:**

— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
25 April 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/97968 A3

(54) Title: HYDROCARBON SYNTHESIS CATALYST AND PROCESS

(57) Abstract: According to the present invention there is provided a hydrocarbon synthesis catalyst comprising a precipitated iron product and a catalyst promotor. The catalyst has a surface area of below 60 m² per gram of catalyst in the reduced form or below 100 m² per gram of catalyst in the non-reduced form. According to the invention there is also provided a process for preparing the catalyst and the use thereof in the synthesis of hydrocarbons.

INTERNATIONAL SEARCH REPORT

International Application No

PCT 01/00084

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C10G2/00 B01J23/78 B01J23/745

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 906 016 A (JOHN HILDRED GEORGE CARLILE;DAVID GALL; SIDNEY LEONARD SMITH) 19 September 1962 (1962-09-19) claims 1,4,11 ---	1-4,11, 12,16, 17, 19-22,25
Y	US 5 118 715 A (FIATO ROCCO A ET AL) 2 June 1992 (1992-06-02) claims 1,2,13 column 8, line 32 - line 37 --- -/-	1-4,11, 12,16, 17, 19-22,25

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *S* document member of the same patent family

Date of the actual completion of the international search

13 February 2002

Date of mailing of the international search report

20/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, O

II INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 01/00084

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 670 476 A (FIATO ROCCO A ET AL) 2 June 1987 (1987-06-02) claims 1,12 column 3, line 40 - line 41 column 4, line 45 - line 47 ---	1,2,4-6, 8-10,21, 22,25
A	US 4 788 222 A (FIATO ROCCO A ET AL) 29 November 1988 (1988-11-29) claims 1,2 column 3, line 57 - line 59 ---	8-10,22, 25
A	GB 733 140 A (RUHRCHEMIE AG;LURGI GES FUER WAERMETECHNIK M) 6 July 1955 (1955-07-06) claims 1,4,7,8,10-12 ---	1-3,7, 11-13, 21,22,25
A	WO 99 49965 A (SASOL CHEMICALS EUROP LTD ;SCHOLTZ JAN HENDRIK (ZA); GIBSON PHILIP) 7 October 1999 (1999-10-07) claim 1 -----	1,2,11, 20,25

II INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/01/00084

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
GB 906016	A 19-09-1962	NONE			
US 5118715	A 02-06-1992	CA GB US US	1236126 A1 2152072 A ,B 4621102 A 4670476 A		03-05-1988 31-07-1985 04-11-1986 02-06-1987
US 4670476	A 02-06-1987	CA GB US US	1236126 A1 2152072 A ,B 5118715 A 4621102 A		03-05-1988 31-07-1985 02-06-1992 04-11-1986
US 4788222	A 29-11-1988	US AU AU CA DE EP NO	4659681 A 588035 B2 5754286 A 1263363 A1 3669445 D1 0202911 A1 860860 A ,B,		21-04-1987 07-09-1989 27-11-1986 28-11-1989 19-04-1990 26-11-1986 21-11-1986
GB 733140	A 06-07-1955	BE NL	514648 A 75045 C		
WO 9949965	A 07-10-1999	ZA AU BR CN EP WO NO PL	9802737 A 9357798 A 9815753 A 1284898 T 1068008 A1 9949965 A1 20004710 A 343169 A1		03-09-1999 18-10-1999 07-11-2000 21-02-2001 17-01-2001 07-10-1999 16-11-2000 30-07-2001